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Fabrication of VO_2-Dispersed Glass in B_2O_3-P_2O_5-V_2O_5 System and Its Thermal Property

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Phase change material (PCM), which enables heat storage based on phase transition, plays an important role for efficient energy utilization. This paper briefly describes our recent study about all-solid PCM by combination of vanadium dioxide (VO_2) with latent heat storage capacity and multicomponent glass, i.e., VO_2-dispersed glass. A B_2O_3-P_2O_5-V_2O_5 glass system is used as a matrix for the VO_2-dispersed glass. An attempt to describe its latent heat storage function is given. Endothermic behavior due to structural phase transition of the VO_2 crystals was observed in the VO_2-dispersed sample, and the transition enthalpy corresponding to latent heat storage capacity was estimated to be $\Delta H \sim 9.5$ J/g. The value of the studied sample was larger than the value of dispersed glass in the BaO-TeO_2-V_2O_5 system that was previously reported. Potential for PCM was considered in the studied sample.

Keywords: glass, vanadium dioxide, latent heat storage, vanadate, thermal property

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INTRODUCTION

Heat storage technology is essential for efficient energy utilization and sustainable development because the technology can appropriately balance the supply and demand amounts of thermal energy for different times and/or spaces (Nomura et al., 2015a). For heat storage, materials able to release the absorbed/conserved energy, i.e., heat storage materials, play a crucial role. Particularly, the latent heat storage is based on the capture or release of energy when a material undergoes a phase change between solid and liquid state, and heat storage materials based on the phase transition are referred to as phase change materials (PCMs) (Hasnain, 1998; Farid et al., 2004; Jacob and Bruno, 2015). For example, ice, paraffin, fatty acids, and inorganic hydrates are frequently utilized as PCMs. However, since the heat storage mechanism of these PCMs involves a solid–liquid phase transition, it is imperative to ensure that the PCM inside the container is maintained in the liquid state. Moreover, damage to the container because of the large volume change occurring during the phase transition and leaking out of the liquid are inevitable. In order to prevent these issues coming from the presence of the liquid state, it is of particular interest to develop new PCMs (Nomura et al., 2015b; Tokoro et al., 2015).

A strongly correlated electron system, vanadium dioxide (VO_2), has gained much interest as a PCM. A reversible solid–solid phase transition occurs at 68°C, accompanying an exothermic or endothermic reaction, and the latent heat of VO_2 is comparable to that of the typical PCMs (Niitaka et al., 2010; Wu et al., 2011). Although VO_2 is commercially available as a powder, if we use the VO_2 powder as PCM, it is mandatory to use a container matrix. Thus, VO_2 exhibits some disadvantages that impede large-scale PCM applications.

Glass exhibits immense advantages from the viewpoint of materials science, e.g., large-scale or mass production, flexibility, and formability (Sakamoto and Yamamoto, 2010). Recently, the authors' group has proposed a new PCM, i.e., VO_2-dispersed glass, where the VO_2 powders embedded in the glass matrix serve as a durable container-free PCM (Muramoto et al., 2018). $30BaO\text{-}10TeO_2\text{-}60V_2O_5$ (in mol%) glass was selected as the matrix on the basis of thermal and water-immersion tests. It was suggested that the Te–O polyhedral units contributed to a three-dimensional network structure of the glass (Ahamad et al., 2012), resulting in its high water resistivity. On the other hand, the deposit amount of Te element is relatively small, being comparable to that of noble metals, and additionally Te, and its related compounds are toxic. Another candidate in the vanadate system, $B_2O_3\text{-}P_2O_5\text{-}V_2O_5$ glass, was also considered, even though it possessed low water resistivity. Nevertheless, $B_2O_3\text{-}P_2O_5\text{-}V_2O_5$ glass consists of much more common and less-toxic substances, i.e., B_2O_3 and P_2O_5, and these oxides possess a considerably low melting temperature compared to that of a typical glass-former, SiO_2. These lead us to consider that VO_2 powder can be incorporated into a $B_2O_3\text{-}P_2O_5\text{-}V_2O_5$ glass without any degradation. Therefore, in this study, we have fabricated VO_2-dispersed glasses by an incorporation technique and then examined the endothermic behavior based on the phase transition of VO_2 crystals.

EXPERIMENT

In this study, the matrix glass with a composition of $15B_2O_3\text{-}10P_2O_5\text{-}75V_2O_5$ (in mol%) was prepared by a conventional melt-quenching technique using an alumina crucible with a lid. Commercial reagent-grade powders of B_2O_3, $(NH_4)_2HPO_4$, and V_2O_5 were used as raw materials. The mixture of the raw materials was melted at 800°C for 60 min under air. The melt was poured onto a steel plate heated at ∼200°C, followed by pressing using another steel plate to obtain the as-quenched sample. The sample was confirmed to be in amorphous state as evidenced by X-ray diffraction (XRD) analysis (Cu-Kα radiation). Subsequently, to fabricate the VO_2-dispersed glass, the incorporation method reported by Komatsu et al. (1995) was employed in the study: A powdered matrix glass and VO_2 powder (purity: 99.9%; Kojundo Chemical Laboratory Co., Ltd.) were mixed using an alumina mortar. Second, the mixture was added into an alumina crucible and melted at 1,200°C for 15 min under air. The quenching process was similar to that utilized during the preparation of the matrix glass, finally furnishing VO_2-dispersed glass.

The state of crystal phase in the dispersed sample was confirmed by XRD analysis and scanning electron microscope (SEM). Prior to XRD measurement, the dispersed samples were powdered by the use of an alumina mortar. The thermal properties of the matrix glass and VO_2-dispersed samples and glass-transition (T_g), crystallization-onset (T_x), and crystallization-peak temperatures (T_p), were examined by differential thermal analysis (DTA; heating rate of 10 K/min, Rigaku Corporation, Thermoplus TG8120). The transition enthalpy (ΔH), which corresponds to the amount of the stored latent heat, of the VO_2-dispersed sample was evaluated by differential scanning calorimetry (DSC; heating rate of 1 K/min, Seiko Instruments Inc., DSC6220). The specific heat, C_p [$= \left(\frac{\partial H}{\partial T}\right)_p$], was measured as a function of temperature (T), and ΔH was estimated on the basis of the thermodynamic relation, i.e., $H = \int C_p dT$. The sample state used in the measurement was the bulk form with a weight of ca. 10 mg.

RESULTS

Characterizations of the VO_2-Dispersed Glass

Prior to fabrication of the VO_2-dispersed sample, the $15B_2O_3\text{-}10P_2O_5\text{-}75V_2O_5$ glass (matrix) was examined. The XRD

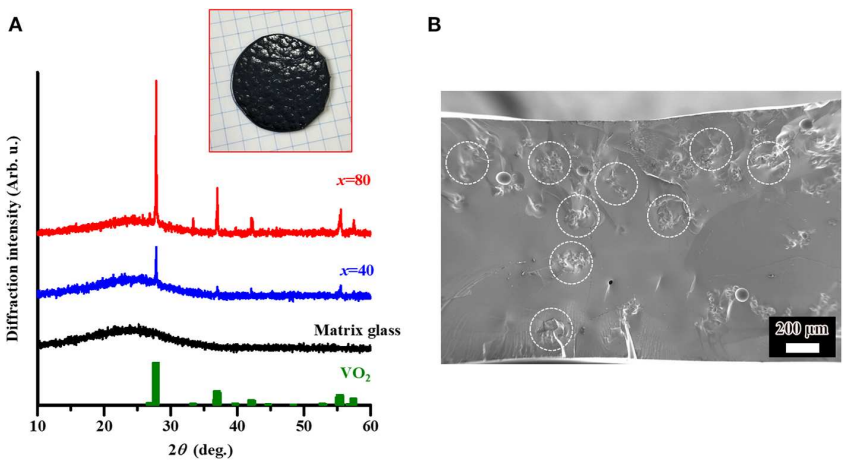

FIGURE 1 | (A) Powder X-ray diffraction (XRD) results of the matrix glass with composition of $15B_2O_3\text{-}10P_2O_5\text{-}75V_2O_5$, and the glasses dispersed with VO_2 powder on the basis of the incorporation method. The values of x represent the additive amount of dispersed VO_2 (in mol%). In addition, the ICDD patterns of VO_2 (43–1051) are included. The inset corresponds to a photo of the dispersed sample with $x = 80$. **(B)** Scanning electron microscope (SEM) image of the cross-section of the dispersed sample with $x = 40$. The encircled region corresponds to the incorporated VO_2 phase.

measurement of the as-quenched sample indicated a halo pattern without any sharp diffraction peaks, which is a characteristic of the amorphous phase (cf. **Figure 1**). We have already obtained the DTA curve of $15B_2O_3$-$10P_2O_5$-$75V_2O_5$ glass (Muramoto et al., 2018), and the parameters could be estimated on the basis of the previous DTA results as $T_g = 225°C$, $T_x = 266°C$, and $T_p = 279°C$. The values of T_g and T_p were almost identical to the values by Choi et al. (Choi and Ryu, 2015).

The VO_2-dispered glasses with different additive amounts (x; mol%) of VO_2 phase, i.e., $15B_2O_3$-$10P_2O_5$-$75V_2O_5$:xVO_2 composites with $x = 40$ and 80, were studied by XRD analysis. As a result, the crystalline diffraction peaks corresponding to VO_2 phase could be observed in combination with the amorphous halo patterns due to matrix glass (**Figure 1A**), and the intensity of diffraction peaks increased with x. In addition, SEM observation was conducted in the sample with $x = 40$ as a representative in order to check the dispersion state in the matrix glass. As a result, we can see the inclusions with a size of ca. 100 μm, i.e., the presence of aggregation of VO_2 particles (**Figure 1B**). The XRD and SEM results suggest that the VO_2 phase is stably incorporated in the matrix glass. A possible explanation of the stable incorporation could be given by an abundance of vanadium around the incorporated VO_2 phase, i.e., saturation of vanadium in the matrix glass, resulting in the suppression of vanadium migration/diffusion from the VO_2 (Muramoto et al., 2018). Furthermore, the melting point of VO_2 (~1,970°C) is much higher than the processing temperature for incorporation (1,200°C). This probably contributes to the stable incorporation as well.

As the result of DTA, the dispersed samples exhibited similar DTA curves to the matrix glass, i.e., endothermic region (224–229°C) and sharp exothermic peaks (280–290°C), which correspond to the T_g and T_p, respectively (**Figure 2**). We have found that the matrix glass crystalizes the V_2O_5 phase by means of thermal treatment at the T_p (Muramoto et al., 2018). In this study, crystallization of the V_2O_5 phase was also confirmed in the dispersed glasses heat-treated at the T_p for 1 h by means of the XRD measurement. Furthermore, we should mention that clear endothermic peaks are observed in the temperature range of ~60–80°C (onset temperature: 63–66°C), which is much lower than the T_g. Since their peaks tend to be large as the increase in x, it is reasonable to consider that the endothermic peaks originate from the phase transition of the dispersed VO_2 phase because of the T_c~68°C. Thus, we have concluded that VO_2-dispersed glass was successfully fabricated in the B_2O_3-P_2O_5-V_2O_5 system. This also leads us to expect that heat storage based on the solid-state phase transition of VO_2 is possible in the dispersed glass sample. Meanwhile, the endothermic peak of the sample with $x = 40$ was relatively smaller than the peak expected from the sample with $x = 80$, in which the amount of the VO_2 phase is double. As a possible explanation, the smallness of the endothermic peak is supposed

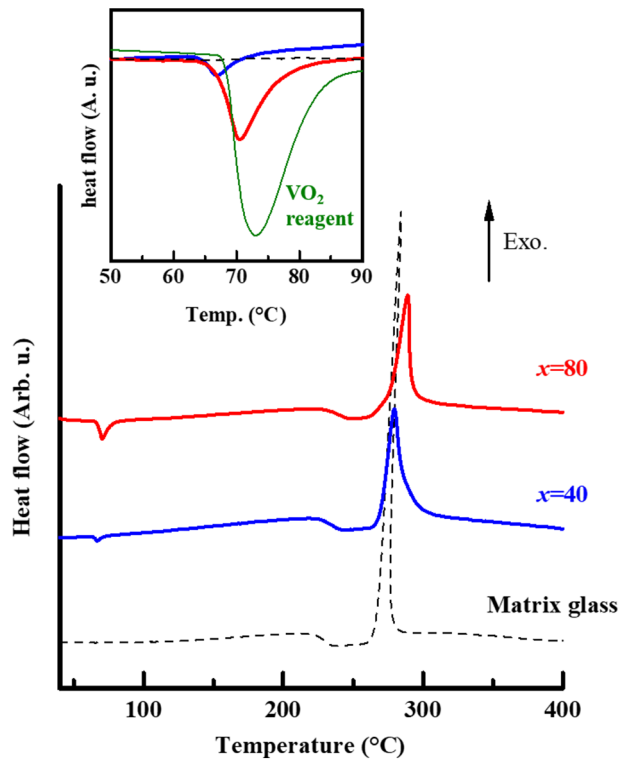

FIGURE 2 | Differential thermal analysis (DTA) results of the dispersed samples, $15B_2O_3$-$10P_2O_5$-$75V_2O_5$:x ($x = 40$ and 80; the studied samples are bulk form), together with the result of matrix glass referred from the paper (Muramoto et al., 2018). The inset shows the DTA curves in a low-temperature region, in which an endothermic reaction was observed in the heating process. The endothermic peaks with onset temperature are around the vicinity of T_c~68°C, indicating the structural phase transition of the dispersed VO_2 phase. The DTA result in the VO_2 reagent used in this study is also included (green curve; peak intensity was reduced to fit the graph).

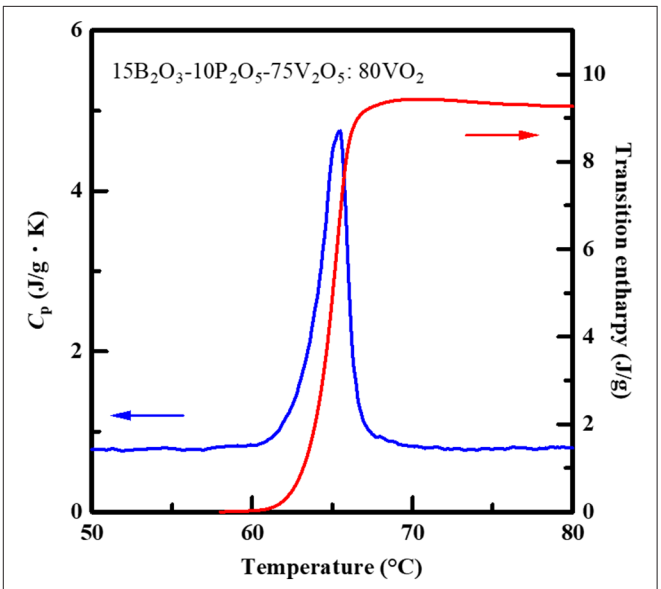

FIGURE 3 | Heat capacity and transition enthalpy for the VO_2-dispersed glass in the B_2O_3-P_2O_5-V_2O_5 system with $x = 80$. The transition enthalpy, ΔH, was obtained by thermodynamic treatment based on $H = \int C_p dT$ because the enthalpy corresponded to the latent heat storage capacity.

to be due to low dispersion of incorporated VO_2 phase in the matrix glass.

Thermal Properties

We have measured the specific heat in the VO_2-dispersed glass with $x = 80$ as a representative sample by means of DSC measurement in order to examine the latent heat storage function. A steep change in the specific heat (peak of the C_p-T curve), related to the phase transition of the dispersed VO_2 powder, was observed around the phase-transition temperature of VO_2 as well as the DTA result, and subsequently, the transition enthalpy (ΔH; the latent heat storage capacity) was estimated to be $\Delta H \sim 9.5$ J/g (**Figure 3**), corresponding to ca. 21% of that of the VO_2 reagent, i.e., ∼45 J/g (Muramoto et al., 2018). Thus, the latent heat storage function is also demonstrated in the dispersed sample in this study. Furthermore, the ΔH value obtained in this study is larger than the value of the VO_2-dispersed sample with same amount of VO_2, i.e., $\Delta H = 8.9$ J/g for the 30BaO-10TeO_2-60V_2O_5:80VO_2 (Muramoto et al., 2018).

DISCUSSION

Vanadate-system glasses are recognized to be synthesized at low melting-process temperature compared to the usual silicate glass. This is quite important for fabrication of the VO_2-dispersed glass in order to prevent the degradation/decomposition of dispersed VO_2 phase due to its transforming into other oxide phases, e.g., Magneli phase (Baldassarre et al., 2007), and to energy saving during the fabrication process. The thermal assessment in this study revealed that, apart from the problem of low water resistivity, the studied B_2O_3-P_2O_5-V_2O_5 system is able to involve the VO_2 powder and to allow its phase transition, which provides a latent heat storage function. In addition, the T_g of the studied glass matrix is lower than that of matrix previously studied; $T_g = 276°C$ for 30BaO-10TeO_2-60V_2O_5 glass (Muramoto et al., 2018), suggesting the re-formability of the dispersed glass after its fabrication.

Barde et al. described a weakness against water in B_2O_3-P_2O_5-V_2O_5 system glass, which is evidenced by DTA (Barde et al., 2015). It is supposed that, under low moisture conditions, the VO_2-dispersed glass in this study works as an all-solid PCM. Otherwise, the addition of other glass constituents, which contributes to the improvement of water resistivity, also seems to be effective for the PCM application because Kubiki et al. reported that the addition of WO_3 provides the strengthening of the glass network in vanadate-system glass, resulting in its high chemical durability (Kubiki et al., 2013). In addition, another point that should be improved is the dispersibility of VO_2 in a glass matrix. The SEM result (**Figure 1B**) suggests that the VO_2 particles are inhomogeneously dispersed in the matrix glass because the size of inclusion is ca. 100 μm despite the size of the VO_2 particle being estimated to be ∼20 μm (Muramoto et al., 2018), i.e., aggregation of VO_2 particles. Irradiation of the ultrasonic wave during the incorporation process may be effective to obtain a well-dispersed sample.

SUMMARY

We already have proposed a new all-solid PCM, i.e., VO_2-dispered glass, and demonstrated the latent heat storage in the BaO–TeO_2-V_2O_5 system. In this study, to avoid the use of Te element, which is a rare metal and is toxic, another candidate vanadate system was considered, i.e., the B_2O_3-P_2O_5-V_2O_5 system, as a matrix glass. We have been able to fabricate the VO_2-dispersed glasses in this system and demonstrated the heat storage function due to the structural phase transition of VO_2. Furthermore, the latent heat storage capacity observed in the studied VO_2-dispersed sample is larger than the capacity of the sample in the BaO-TeO_2-V_2O_5 system, suggesting the potential of all-solid PCM application.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

KM fabricated and characterized the materials. YT, NT, and TF designed the study. YY and SS contributed to the thermal analysis. and YT and TF wrote the paper.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.